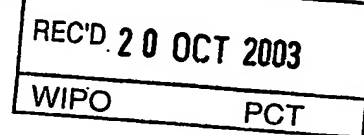




Europäisches
Patentamt

European
Patent Office

Office européen
des brevets



Bescheinigung

Certificate

Attestation

Die angehefteten Unterla-
gen stimmen mit der
ursprünglich eingereichten
Fassung der auf dem näch-
sten Blatt bezeichneten
europäischen Patentanmel-
dung überein.

The attached documents
are exact copies of the
European patent application
described on the following
page, as originally filed.

Les documents fixés à
cette attestation sont
conformes à la version
initialement déposée de
la demande de brevet
européen spécifiée à la
page suivante.

Patentanmeldung Nr. Patent application No. Demande de brevet n°

02078543.2

**PRIORITY
DOCUMENT**
SUBMITTED OR TRANSMITTED IN
COMPLIANCE WITH RULE 17.1 (a) OR (b)

Der Präsident des Europäischen Patentamts;
Im Auftrag

For the President of the European Patent Office

Le Président de l'Office européen des brevets
p.o.

R C van Dijk

BEST AVAILABLE COPY



Anmeldung Nr:
Application no.: 02078543.2
Demande no:

Anmeldetag:
Date of filing: 28.08.02
Date de dépôt:

Anmelder/Applicant(s)/Demandeur(s):

Umicore
Rue du Marais 31
1000 Brussels
BELGIQUE
Ocas n.v.
John Kennedylaan 3
9060 Zelzate
BELGIQUE

Bezeichnung der Erfindung/Title of the invention/Titre de l'invention:
(Falls die Bezeichnung der Erfindung nicht angegeben ist, siehe Beschreibung.
If no title is shown please refer to the description.
Si aucun titre n'est indiqué se référer à la description.)

Zinc alloy bath for hot-dip galvannealing of steel

In Anspruch genommene Priorität(en) / Priority(ies) claimed / Priorité(s)
revendiquée(s)
Staat/Tag/Aktenzeichen/State/Date/File no./Pays/Date/Numéro de dépôt:

Internationale Patentklassifikation/International Patent Classification/
Classification internationale des brevets:

C23C2/00

Am Anmeldetag benannte Vertragsstaaten/Contracting states designated at date of
filing/Etats contractants désignées lors du dépôt:

AT BE BG CH CY CZ DE DK EE ES FI FR GB GR IE IT LI LU MC NL PT SE SK TR

Zinc alloy bath for hot-dip galvannealing of steel

The present invention relates to a hot-dip coating bath composition suitable for galvannealing steel sheet, in particular on coating lines manufacturing alternatively galvanised and the galvannealed products.

Galvannealed coated products are well known to the automotive industry as product with excellent properties. Weldability and paint adhesion are particularly good. Nevertheless, market needs result in that most coating lines produce alternatively galvanised and galvannealed products.

During continuous hot-dip galvanising of steel sheet, a bath of molten zinc is employed. Prior to entering the bath, the sheet typically undergoes a preparatory heat treatment in a furnace with a reducing atmosphere. A so-called snout makes the connection between this preparatory furnace and the coating bath. After passing through the bath, the desired coating thickness is obtained by means of air knives.

When galvannealing is contemplated, the steel sheet undergoes an additional heat treatment in an annealing furnace so as to perform the diffusion of Fe into the Zn coating. This heat treatment is applied immediately after the hot-dip step and the operation of the air knives.

For the manufacture of galvanised as well as galvannealed products, Al is typically added to the molten zinc bath for controlling Fe-Zn alloy growth during the passage of the steel sheet through the bath. The Al forms an intermetallic $Fe_2Al_5Zn_x$ layer at the steel/zinc interface. According to the Al concentration in the bath, the intermetallic layer partially or fully inhibits the Fe-Zn reaction.

For the production of galvanised steel, 0.16 to 0.3 wt.% Al is normally used. This relatively high concentration ensures the formation of a dense intermetallic $\text{Fe}_2\text{Al}_5\text{Zn}_x$ layer, effectively
5 inhibiting the formation of any Fe diffusion into the Zn coating and thus the formation of a Zn-Fe alloy.

The main advantage of this relatively high concentration of Al is that the formation of Fe-Zn compounds is avoided. The
10 surface quality of the product is therefore excellent and the bath remains free of bottom dross, i.e. intermetallic Fe-Zn compounds which form at lower Al contents in the bulk of the bath and which have a tendency to sink to the bottom. Some top dross, i.e. dross floating on the bath surface, is formed; this
15 type of dross is however easy to deal with as it can readily be skimmed off from the surface.

For the production of galvannealed steel however, a permeable inhibition layer is needed. Indeed, while the Fe-Zn alloy
20 should not form significantly during the hot-dip step so as to allow for coating thickness control by the air knives, the Fe-Zn alloy should be rapidly obtained during the subsequent annealing step. To achieve this compromise, the amount of Al has to be kept at the relatively low level of 0.1 to 0.15 wt.%.
25 An intermetallic layer of $\text{Fe}_2\text{Al}_5\text{Zn}_x$ is then obtained which partially covers the steel/zinc interface.

The compromise sought between formation of bottom dross at too low Al contents, and the formation of a too dense inhibition
30 layer at high Al content, renders the optimal Al concentration extremely critical. Moreover, the relatively low amount of Al, which has to be chosen, entails significant drawbacks. In practice, bottom dross formation is unavoidable and typically accounts for a very significant loss of Zn. Further problems
35 linked to the low Al concentration are:

3

- accelerated corrosion of the immersed equipment;
- bottom dross entrapment on the steel sheet;
- deposition of intermetallic compounds on the immersed equipment, in particular on the rolls.

5

The Al concentration problem is further exacerbated when a manufacturer needs to switch between galvanising and galvannealing. Conventionally, two different methods are used to cope with the need to change the Al content of the bath when switching between both processes.

10

A first method is to provide two different baths. The drawbacks of this procedure are the higher equipment cost and the reduced flexibility of the line.

15

A second method is to use a single bath and to change its Al content according to the particular process applied. Main drawbacks of this procedure are the unavoidable concentration inhomogeneities in the bath and the impossibility to maintain a high coating quality during process changes. The elevation of the Al concentration when switching from galvannealing to galvanising results in the conversion of bottom dross into floating dross. Floating dross particles are picked-up by the rolls in the bath and transferred to the surface of the sheet, producing pimples and print-through defects.

20
25

WO0031311 describes a process whereby the same Al level of less than 0.15 wt.% is used when galvanising and galvannealing. As explained later, such a relatively low Al content entails significant drawbacks. Moreover, the decreased bath temperature needed to decrease the iron solubility is doubtfully feasible on a real production line. Also, the use of extra circulation in the bath may enhance the dross pick-up by the rolls.

30

Other patents or patent applications like WO0155468, EP1070765

35

and JP3166352 focus more on the mechanical design of the galvanising bath and on methods to remove the dross in order to solve the dross-related problems.

- 5 Some authors describe possibilities to increase the alloying kinetics, especially by modifying the steel surface in order to enhance the Fe-Zn reaction after the breakdown of the $\text{Fe}_2\text{Al}_5\text{Zn}_x$ intermetallic layer. JP8291379 and JP4254530 describe the use of the so-called pre-oxidation and subsequent reduction,
10 during which a reactive metallic surface layer is created.

It is an object of this invention to provide for a Zn alloy bath especially designed to overcome the above mentioned problems.

15

According to the invention, a process is provided for coating steel, comprising either the steps of:

- galvanising a first quantity of steel by hot-dipping in a Zn alloy bath;
- 20 - switching to galvannealing, whereby a second quantity of steel is hot-dipped in the Zn alloy bath and the coated steel hereby produced is subjected to a thermal treatment in an annealing furnace; or,
- galvannealing a first quantity of steel by hot-dipping in a
25 Zn alloy bath and subjecting the coated steel hereby produced to a thermal treatment in an annealing furnace;
- switching to galvanising, whereby a second quantity of steel is galvanised by hot-dipping in the Zn alloy bath;

whereby the Zn alloy bath contains at least 0.16 wt% Al and is
30 maintained at a constant composition.

In this process, the Zn alloy bath may contain 0.16 to 0.4 wt.% Al and 0.05 to 0.35 wt.% Cr.

5

Preferably, the Zn alloy bath may contain 0.23 to 0.29 wt.% Al and 0.05 to 0.35 wt.% Cr, and more preferably at least 0.1 wt.% Cr. The remainder of the bath can consist of Zn and unavoidable impurities.

5

Another embodiment of the invention covers a process for hot-dip galvannealing steel, comprising the steps of:

- hot-dipping the steel in a Zn alloy bath; and,
- annealing the thereby obtained coated steel, using a Zn bath containing 0.16 to 0.4 wt.% Al and 0.05 to 0.35 wt.% Cr.

- 15 A further embodiment concerns the process of lowering the specific energy consumption of a furnace used for annealing a product which has been hot-dipped in a Zn alloy bath, by performing either one or both steps of:
- lowering the surface temperature of the hot-dipped product in the annealing furnace; or,
 - lowering the residence time of the hot-dipped product in the annealing furnace, whereby Cr is added to the Zn alloy bath.
- 20 Preferably, the bath contains, after addition of Cr, 0.1 to 0.4 wt.% Al and 0.005 to 0.35 wt.% Cr. More preferably, the bath contains at least 0.05 wt.% Cr. The remainder of the bath can consist of Zn and unavoidable impurities.

- 25 It should be noted that the mentioned concentrations correspond to the bulk analysis of the bath, i.e. including undissolved floating compounds.

- 30 The addition of Cr thus changes the alloying kinetics during the galvannealing treatment by weakening the intermetallic layer present at the steel/zinc interface. This allows for a relatively high and uncritical Al concentration for the manufacture of galvannealed product. Although some top dross may be formed, bottom dross, which is as explained above a

serious inconvenient, is avoided. This high Al concentration can be maintained constant for both galvanising and galvannealing.

- 5 The invention also provides for the following additional advantages.

For the production of galvannealed steel sheet, a certain specific energy input is needed during the annealing step to
10 obtain the desired Fe-Zn alloying degree. In an existing installation, the annealing furnace may have become the limiting factor in the quest for a maximal line throughput. In such a situation, the present invention may be helpful: the enhanced diffusion rate of Fe allows for a lower annealing
15 temperature for a given residence time, a shorter residence time for a given temperature, or a lowering of both the residence time and the temperature.

Another advantage of the invention is appreciated when dealing
20 with steels normally requiring an excessively high annealing temperature. This is the case e.g. for high-strength Si and P rich steels. The invented process accelerates the diffusion of Fe, thereby allowing for much lower and reasonable annealing temperatures.

25

Finally, it should be noted that Cr is an ecologically acceptable element, in particular when present in its elemental form such as in an alloy.

30 As a result of research carried out in order to resolve the above mentioned problems, the inventors have discovered that when Cr is introduced into a Zn-Al coating bath comprising Al from 0.1 wt.% to 0.4 wt.%, the inhibition layer is modified. As a matter of fact, it was discovered that this inhibition layer,

normally consisting in $\text{Fe}_2\text{Al}_5\text{Zn}_x$ intermetallic crystals located at the interface between the steel sheet and the Zn overlay, is changed into a two-phased layer. In addition, it has been established that the composition of this two-phased layer can be classified into two different types, called Type I and Type II, as a function of the amount of Cr added to the Zn-Al coating bath.

In a Zn-Al-Cr coating bath comprising Al from 0.1 wt.% to 0.4 wt.% and Cr from 0.005 wt.% to 0.1 wt.%, the two-phased layer Type I is formed at the interface between the steel sheet and the Zn overlay. This two-phased layer Type I consists of both $\text{Fe}_2\text{Al}_5\text{Zn}_x$ and $\text{CrZn}_{13}/\text{CrZn}_{17}$ intermetallic crystals. These $\text{CrZn}_{13}/\text{CrZn}_{17}$ intermetallic crystals are located in the $\text{Fe}_2\text{Al}_5\text{Zn}_x$ crystals or between the $\text{Fe}_2\text{Al}_5\text{Zn}_x$ intermetallic crystals and the Zn overlay.

For the galvannealing treatment of coated steel sheets, it has been noted that, in comparison with the $\text{Fe}_2\text{Al}_5\text{Zn}_x$ inhibition layer, this two-phased layer allows a faster Fe diffusion into the Zn overlay. The most pronounced effects have been measured for a Zn-Al-Cr coating bath comprising Al from 0.22 wt.% to 0.35 wt.% and especially from 0.23 wt.% to 0.29 wt.%, with Cr from 0.05 wt.% to 0.1 wt.%.

25

In a Zn-Al-Cr coating bath comprising Al from 0.1 wt.% to 0.4 wt.% and Cr from 0.1 wt.% to 0.35 wt.%, the two-phased layer Type II is formed at the interface between the steel sheet and the Zn overlay. This two-phased layer Type II consists of $\text{Fe}_2\text{Al}_5\text{Zn}_x$ and $\text{Cr}_2\text{Al}_3\text{Zn}_x$ intermetallic crystals. These $\text{Cr}_2\text{Al}_3\text{Zn}_x$ intermetallic crystals are located between the $\text{Fe}_2\text{Al}_5\text{Zn}_x$ intermetallic crystals and the Zn overlay. This two-phased layer also allows for a faster Fe diffusion into the Zn overlay during galvannealing. The most pronounced effects have been measured for a Zn-Al-Cr coating baths comprising Al from 0.22

wt.% to 0.35 wt.% and especially from 0.23 wt.% to 0.29 wt.% and Cr from 0.1 wt.% to 0.35 wt.%.

5 If Cr is added into a Zn-Al coating bath containing less than 0.1 wt.% Al, the intermetallic crystals formed at the interface between the steel sheet and the zinc overlay are not modified. The same can be observed when less than 0.005 wt.% Cr is added to the Zn-Al coating bath.

10 If the Cr content is higher than 0.35 wt.% or the Al content is higher than 0.4 wt.% in the coating bath, it has been established that process or product problems occur, such as Cr solubility problems.

15 It has also been established that the two-phased Type II layer is more effective during the galvannealing treatment than the Type I two-phased layer, allowing therefore the fastest Fe diffusion in the zinc overlay. Consequently, the optimal composition of the Zn-Al-Cr coating bath is as follows: from 20 0.23 wt.% to 0.29 wt.% Al, from 0.1 wt.% to 0.35 wt.% Cr, the remainder being Zn, Fe and the unavoidable impurities.

25 The amount of Fe diffused into the coating is a measure for the annealing reactivity. Typical values are in the range between 9 and 11 % of Fe, corresponding to an Fe content in the coating of 4.5 to 5.5 g/m² for an assumed coating thickness of 7 µm.

30 As a first example, annealing reactivity data is produced for a typical cold-rolled multi-phase steel with, in wt.%, 0.12 C, 0.12 Si, 1.5 Mn, 0.25 Cr and 0.2 Mo. The Fe content in the coating was determined for a classical galvannealing bath and for a bath according to the invention. Table 1 shows that a significantly higher reactivity is obtained with the Cr-bearing bath according to the invention: the reactivity increases with

about 60 %, even though a significantly lower annealing temperature was used.

Table 1: Annealing reactivity vs. bath composition

Bath (wt.%)	Process	Reactivity (g/m ² Fe in coating)
0.135 Al; no Cr	20 sec.; 550 °C	4.11
0.135 Al; 0.07 Cr	20 sec.; 530 °C	6.70

5

As a second example, annealing reactivity data is shown for a classical Ti-IF steel with approximately 0.002 wt.% C, 0.17 wt.% Mn and 0.04 wt.% Ti, the other elements being the normal impurities in steel. The annealing conditions were 30 sec. at 480 °C, which are typical for industrial lines. Figure 1 gives the Fe-content in the coating vs. the Cr-content in the coating bath. It follows that an increase of approximately 3 g/m² of Fe is obtained for each 0.1 wt.% Cr added to the bath, both for 0.2 wt.% Al (a conventional galvanising bath) as for 0.13 wt.% Al (a conventional galvannealing bath). The typical minimum level of 4.5 g/m² of Fe in the coating is thus reached, using a coating bath with 0.2 wt.% Al and a Cr-content of at least 0.05 wt.%. This Cr-content is therefore sufficient to use a classical galvanising bath composition in a galvannealing process.

Claims

1. Process for coating steel, comprising either the steps of:
 - galvanising a first quantity of steel by hot-dipping in a Zn alloy bath;
 - switching to galvannealing, whereby a second quantity of steel is hot-dipped in the Zn alloy bath and the coated steel hereby produced is subjected to a thermal treatment in an annealing furnace; or,
 - galvannealing a first quantity of steel by hot-dipping in a Zn alloy bath and subjecting the coated steel hereby produced to a thermal treatment in an annealing furnace;
 - switching to galvanising, whereby a second quantity of steel is galvanised by hot-dipping in the Zn alloy bath;
- characterised in that the Zn alloy bath contains at least 0.16 wt% Al and that its composition is kept constant
2. Process according to claim 1, characterised in that the Zn alloy bath contains 0.16 to 0.4 wt.% Al and 0.05 to 0.35 wt.% Cr
3. Zn alloy bath for hot-dip galvannealing steel, characterised in that it contains 0.23 to 0.29 wt.% Al and 0.05 to 0.35 wt.% Cr
4. Zn alloy bath for hot-dip galvannealing steel according to claim 3, characterised in that it contains at least 0.1 wt.% Cr
5. Zn alloy bath for hot-dip galvannealing steel according to any one of claims 2 to 4, characterised in that it further only contains Zn and unavoidable impurities
6. Process for hot-dip galvannealing steel, comprising the steps of:

11

- hot-dipping the steel in a Zn alloy bath; and,

- annealing the thereby obtained coated steel;

characterised in that the Zn bath contains 0.16 to 0.4 wt.% Al and 0.05 to 0.35 wt.% Cr, the remainder being Zn and

5 unavoidable impurities

7. Process of lowering the specific energy consumption of a furnace used for annealing a product which has been hot-dipped in a Zn alloy bath, by performing either one or both steps of:

10 - lowering the surface temperature of the hot-dipped product in the annealing furnace; or,

- lowering the residence time of the hot-dipped product in the annealing furnace;

whereby Cr is added to the Zn alloy bath

15

8. Process according to claim 7, characterised in that, after addition of Cr, the Zn alloy bath contains 0.1 to 0.4 wt.% Al and 0.005 to 0.35 wt.% Cr

20 9. Process according to claim 8, characterised in that, after addition of Cr, the Zn alloy bath contains at least 0.05 wt.% Cr

25 10. Process according to claim 6 or any one of claims 7 to 9, characterised in that the Zn alloy bath further only contains Zn and unavoidable impurities

AbstractZinc alloy bath for hot-dip galvannealing of steel

- 5 The present invention relates to a hot-dip coating bath composition suitable for galvannealing steel sheet, in particular on coating lines manufacturing alternatively galvanised and the galvannealed products.
- 10 The addition of Cr to the bath allows manufacturers to switch between galvannealing and galvanising using the same bath composition, while the Al level is maintained at or above 0.16 wt. %.
- 15 The addition of at least 0.005 wt. % of Cr to the bath also allows to lower the annealing temperature and to shorten the residence time of the steel in the annealing furnace.

1/1

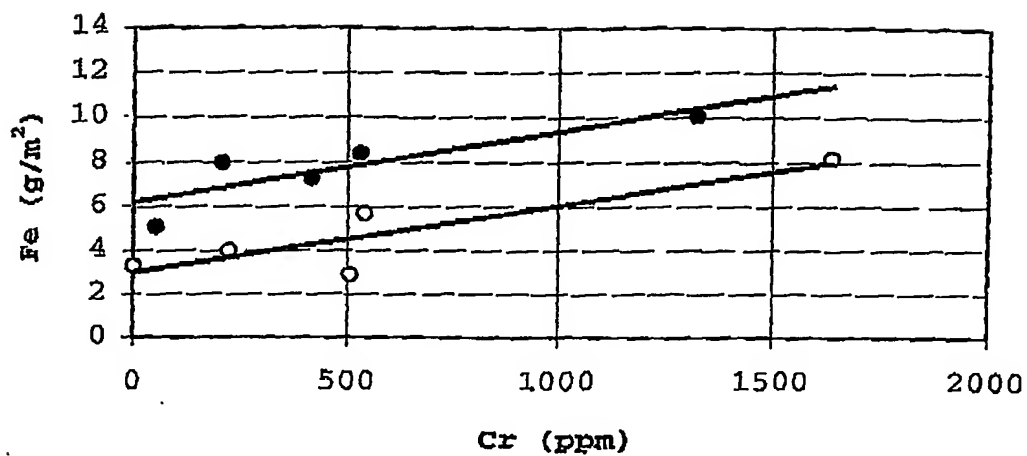


Figure 1: Fe-content in the coating vs. the Cr-content in a bath with an Al level of 0.2 (○) and 0.13 wt% (●)

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ BLACK BORDERS
- ☐ IMAGE CUT OFF AT TOP, BOTTOM OR SIDES
- ☐ FADED TEXT OR DRAWING
- ☐ BLURRED OR ILLEGIBLE TEXT OR DRAWING
- ☐ SKEWED/SLANTED IMAGES
- ☐ COLOR OR BLACK AND WHITE PHOTOGRAPHS
- ☐ GRAY SCALE DOCUMENTS
- ☐ LINES OR MARKS ON ORIGINAL DOCUMENT
- ☒ REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY
- ☐ OTHER: _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.